# Sonochemical Oxidation of Cyanide Using Potassium Peroxydisulfate as an Oxidizing Agent

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## Introduction

Free cyanide is a singly charged anion containing unimolar amounts of carbon and nitrogen atoms triply bonded together: C_N_ (bond energy: 891 kJ_mol_1) or CN_. The triply bonded cyanide is a strong ligand, capable of complexing even at low concentrations with any heavy metal. Since the health and survival of plants and animals are dependent on the transport of heavy metals through their tissues, cyanide is very toxic in an ecosystem when it is complexed with heavy metals. The mean lethal dose for a human adult is between 50 and 200 mg.[1] Owing to toxicity concerns, the United States Environmental Agency (U.S. EPA) is regulating total cyanide for drinking and aquaticbiota waters at 200 and 50 _g_L_1, respectively.[2] Free cyanide refers to the most toxic forms of cyanide: cyanide anion and hydrogen cyanide. Weak-acid dissociables (WADs) refer to cyanide complexes with metals such as cadmium, copper, nickel, and zinc. Although thiocyanate [S–C_N_ (S–C and C_N bond energy: 272 and 891 kJ_mol_1)] or SCN_ is a type of WAD, it is often considered in its own category. Strong acid dissociables (SADs) refer to cyanide-complexes with metals such as Co, Au, Fe, and Ag. Although toxicity differs according to cyanide species, cyanide could cause a significant problem of eutrophication when it is released into a water system and partially oxidizes into $NO_2$_/$NO_3$_. The advanced oxidation process (AOP) using UV radiation in combination with various oxidants such as $H_2O_2$, Fenton's reagent, and ozone, shows significant potential for treating toxic compounds, which are refractory in nature and difficult to be oxidized completely by conventional methods.[3,4] Among the AOPs, a mediated oxidation is needed to describe the meaning of this word, which also plays an important role because it can decompose most organic and inorganic compounds. Although the rate of chemical oxidation in the presence of PDS is relatively slow at room temperature,[5] PDS can be readily decomposed into sulfate anion radicals by sonochemical, photolysis, or thermal decomposition.[6] Moreover, $\cdot SO_4^-$ (E ¼ 3:1 V) has a higher oxidation potential than the most common oxidant, hydroxyl radicals, $\cdot OH$ (E ¼ 2:72 V).[7] Therefore, an active interest is currently being taken in the sulfate radical-based AOPs.

Sonochemistry has attracted attention among the AOP methods used in remediation processes because of its simple

operational requirements and its potential application using by simple oxidants.[8] In addition, sonochemical oxidation can be operated under ambient conditions and is a safer technique than UV and ozonation. A technology capable of oxidizing cyanide completely is necessary because the silent toxicity by $NO_3^-$ could occur when cyanide is not completely oxidized into $N_2$ and $CO_2$ gases. Owing to the strong oxidation capacity, sonochemical oxidation can be considered a methodology to oxidize cyanide completely. Up to now, the PDS assisted oxidation of cyanides using the sonochemical method has not been reported. In this study, the $CN^-$ and $SCN^-$ mineralization, kinetics, and mechanism of ultrasonic oxidation mediated by PDS (designated as US/PDS) were investigated.

## Materials and Methods

### 2.1 Chemicals and reagents

Reagent-grade chemicals and deionized (DI) water were used for the preparation of all solutions used in this study. The reagent-grade potassium cyanide (KCN) in 0.1% NaOH was obtained from Alfa Aear. Potassium thiocyanate (KSCN) and potassium persulfate (PPS; $K_2S_2O_8$) were purchased from Sigma-Aldrich (purity, 99%).

### 2.2 Reactor setup

The sonoreactor of a glass cup-horn-type with 1 L capacity equipped with a cup-horn type ultrasonic transducer (Mirae Ultrasonic MEGA-100). The diameter of each transducer was 10 cm. The applied frequency was 450 kHz and a maximum power (100 W) was applied for 500mL of solution using a single piezoelectric transducer (PZT; Tamura).[9,10] The temperature in the solution was measured using a thermometer (Tecpel DTM-318) at several locations during ultrasound irradiation, and the ultrasonic power was modified by the calorimetry method.[11]

### 2.3 Analytical methods

The TOC concentrations of $CN^-$ and $SCN^-$ were measured with a TOC analyzer (GE Sievers 5310C and Sievers 900 Autosampler). Cyanate ($OCN^-$) concentration was determined by hydrolyzing cyanate to ammonia at an acidic pH (1.5–2.0), and ammonia concentration was measured by the Nesslerisation method. The amounts of $SO_4^{2-}$ and $NO_3^-$ released in the solution were determined by ion chromatography (IC; Dionex DX500).

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